

Gasification of Lignin from Rice Straw

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Abstract

Gasification of Lignin from Rice Straw. Denisse Arroyo (University of Puerto Rico, Mayagüez, P. R. 00680) Steven Phillips (National Renewable Energy Laboratory, Golden, CO 80401)

The deterioration of fossil fuels reserves and environmental considerations have led to a resurgence in research and development studies into alternative fuel supplies. An important study is the lignocellulosic biomass ethanol production, which has lignin as an unfermentable residue. Another study is the gasification process, a method of converting biomass into a mixture of gases. This research consists of the lowering of the moisture content and the characterization of the gasification process of residues from rice straw that came from an ethanol plant. A meat grinder and a drier oven were used to lower the moisture content from 78 to 13%. For the gasification process a fluidized bed reactor at 600-750 °C and a thermal cracker at 700-800 °C were used in order to make the reaction take place. After exiting the thermal cracker, the entire stream enters a condensation train where the temperature is decreased to between 20 and 30°C and the noncondensable gases are analyzed using a GC. The amount of feedstock gasified fluctuated between 24 to 41%, given that the feedstock consisted of 40% ash. The amount of gasification products increased with temperature increasing.

Research Category

ERULF: Physics Chemistry Biology Engineering Computer Science
CCI: Bionotechnology Environmental Science Computing

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Introduction

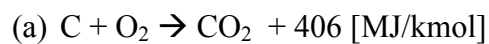
The deterioration of fossil fuels reserves and environmental considerations have led to a resurgence in research and development studies into alternative fuel supplies. One attractive option is the gasification process, a method of converting raw biomass into a mixture of gases, which have the potential to be burnt in combustion engines for the production of electricity. (Rapagna, 1997)

Biomass is an organic material derived from plant and animal material. It has the potential, when combined with oxygen to release heat. Biomass material is composed of three important constituents: cellulose, lignin, and hemicellulose. Lignin represents about 25% of lignocellulosic biomass. Lignin is a by-product of chemical pulping processes and is also likely to become available as an unfermentable residue from lignocellulosic biomass ethanol production. Any ethanol production process will have lignin as a residue. Adding value to this residue will significantly enhance the competitiveness of biomass-to-ethanol conversion.

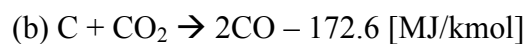
Gasification is a thermal process converting dry biomass feedstock into a mixture of gases that can be burnt in internal combustion engines and gas turbines. The gasification process takes place in a sealed container with a restricted supply of air. Gasification process can be done in a fluidized bed gasifier. Fluidized beds have good heat and material transfer between the gas and solid phases with good temperature distribution, high specific capacity and fast heat-up. They tolerate wide variations in fuel quality and a broad particle-size distribution. Disadvantages of fluidized beds are high dust content in the gas phase and the conflict between high reaction temperatures with good conversion efficiency and low melting points of ash components. (Warnecke, 2000)

The gasification process can be broken down into three phases. The first phase is a process of pyrolysis during which the biomass is converted by heat into charcoal and volatile compounds, such as steam, methanol, acetic acids and tars. The second phase is an exothermic reaction in which part of the carbon is oxidized to carbon dioxide. In the third phase, part of the carbon dioxide, the volatile compounds and the steam are reduced to carbon monoxide, hydrogen and methane. This mixture of gases diluted with nitrogen from the air and unreduced carbon dioxide is known as producer gas.

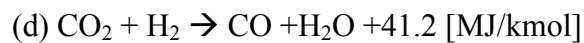
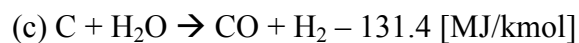
The conversion process from solid biomass to producer consists of an initial combustion reaction (a), which occurs in the reactor, nearest the air inlet.



The carbon dioxide produced in this first reaction is then, in the presence of glowing carbon, reduced to carbon monoxide (b). When the gasifier is first lit, the level of carbon dioxide is at its highest. The quality of the producer gas increases with the increase in reactor temperature and size.



Other reactions that take place in the third phase are:



The aim of the present work is to characterize the gasification process of lignin from rice straw that came like residues from lignocellulosic biomass ethanol production. An important aspect to take in consideration is the moisture content of the feedstock. The moisture content of the most biomass fuel depends on the type of fuel, its origin and treatment before it is used for

gasification. Moisture content of the fuel is usually referred to inherent moisture plus surface moisture. The moisture content below 15% by weight is desirable for trouble free and economical operation of the gasifier. Higher moisture contents reduce the thermal efficiency of gasifier and results in low gas heating values. Igniting the fuel with higher moisture content becomes increasingly difficult, and the gas quality and the yield are also poor.

Another aspect to take in consideration is the particle size. The fuel size affects the pressure drop across the gasifier and power that must be supplied to draw the air and gas through gasifier. Large pressure drops will lead to reduction of the gas load in downdraft gasifier, resulting in low temperature and tar production. Excessively large sizes of particles give rise to reduced reactivity of fuel, causing start-up problems and poor gas quality.

Materials and Methods

The gasification process diagram is shown in figure #1. The feedstock used was residues that came from an ethanol plant. The plant used rice straw as the biomass. This residues were composed primarily of lignin. Initially, this biomass had a moisture content of 78% (by weight). To lower the moisture content, the feed was dried until a moisture content of 5-30% was obtained. At the beginning of each run the reactor was filled with sand (silica sand 50-80 mesh, 297-177 micron) to 5 inches in depth. Inside the reactor, the feed mixes with the sand to undergo thermal reactions. The sand is maintained in a fluid-like phase by superheated steam that flows into the bottom of the reactor through a sintered-metal distribution plate. The entire reactor is heated by electrical heaters controlled with an Omega PID temperature controller. The fluidizing gas stream sweeps reaction products (a mixture of vapors, gases, and solids) out of the reactor. A

cyclone was connected to the exit of the disengagement section to capture the solid particles escaping from the bed. The solids, consisting of mostly char, sand and other non reactive mineral matter, are collected in a receiver attached to the bottom of the cyclone. The remaining products continue on to the thermal cracker where a higher operating temperature and longer residence time can cause additional reactions to occur. The fluidizing column, cyclone and thermal cracker were insulated using a kaowool blanket to reduce heat loss from the system.

After exiting the thermal cracker, the entire stream enters a condensation train where the temperature is decreased to between 20 and 30⁰C. The condensation train consist of circulating water cooled with a heat exchanger, a chilled cyclone and a spray scrubber. Species with dew points above this temperature are condensed. Any entrained solids are also removed in this operation. Aerosols and non-condensables gases leaves the condensation train and enter the gas polishing section. The gas is “polished” using a coalescing filter to remove entrained aerosols. The non-condensable gases are vented to a thermal oxidizer. A sliptream of the gas is sampled automatically by a gas chromatograph (GC) for analysis.

For the first experiment the feedstock was pelletized using a meat grinder wrapped with a heating tape and a hot air gun blowing on the feed as it left the grinder. The average sizes of the pellets were 1/8-in. diameter and ¾ in. length with moisture content of 13%. The system was heated to a temperature of approximately 600 °C for the reactor bed and 700 °C for the thermal cracker. Steam was used as a carrier gas at a rate of 2 kg/hr. The lignin pellets were fed at a rate of 0.65kg/hr.

Figure #2 shows the temperature profile of the system during the experiment. The experiment was started at 2:20 p.m. After an hour the system was turned off to check the feeder, because apparently it was not feeding. The system was turned on again and set to a higher bed

reactor and thermal cracker temperature of 650 °C and 850 °C, respectively. The feeder was turned on again at 4:32 p.m. The temperature of the bed was increased to 700 °C because the heater controller was not operating properly. The system was shutdown at 5:45 p.m.

For the second experiment the meat grinder was used, but this time everything was put in a tray and dried in a dryer oven. It had a size of approximately 1/8 in with a moisture content of 27%. We fed at approximately 1.0 kg/hr. The system was heated until a temperature of 850°C for the thermal cracker exit and 600 °C in the fluidized reactor was reached. In order to improve the sampling procedure, a molecular sieve column was placed at the syngas exit. This was done to reduce the amount of water going to the GC. The experiment was started at 1:17 p.m. At 3:36 the molecular sieve column was removed to see if it had an effect in the analysis of the syngas. The experiment ran until the feed was over; this happened at 5:50 p.m. Figure #6 shows the temperature profile of the system during this experiment.

The experiment #3 was performed with the objective of analyzing tars and minor components of the syngas with a molecular beam mass spectrometer (MBMS). The changes in concentrations were recorded to see how the changes of parameters affected them. The fluidized bed reactor and thermal cracker were operated to 600 °C and 850 °C, respectively. Air was fed to the reactor at a rate of 5 to 2 slpm to see what effects it had on the gas concentration leaving the process. The experiment was also run with no air and the feed was changed to oak wood. The exit syngas was analyzed with the GC. Figure #11 shows the temperature profile during the experiment # 3.

Results

After a careful study of the data and a mass balance in the gasification system; using some numerical integration techniques, we determined what happened with the original feed. This is shown Figure #5. In this figure we can see that 41% of our original feed was gasified.

Figures #3 and #4 show the results of the gas chromatograph (GC). These graphs were normalized to a nitrogen free basis, because N_2 is one of the gases that we are indirectly feeding to the system and it is not one of the gasification products. During the experiment, we can see that the concentration went down when we turned off the feeder, and how the different components of the gas went to higher percentages when the temperatures of the reactor bed and the thermal cracker.

After the experiment we performed a residuals solid mass balance. Table #1 reports in which parts of the system the solids were recovered. The total feed was 1.8 Kg and we produced around 0.72 Kg of syngas.

Table #2 reports where we recovered most of the water. We recovered a total of 29.71 Kg. We put originally 10 kg of water and we fed a total of 25 Kg of steam that condensed. In our complete mass balance we put approximately 37.52 Kg, and we recovered 30.545 Kg.

For our second experiment we performed a mass balance and analysis of the feed and exit products; the results are shown in table #3. Figures #7 and #8 show the composition of the exit gas. At the beginning of the experiment we put a molecular sieve column to remove the moisture that was going to the GC. After looking at the composition of the exit gas, we saw that there was oxygen that should not be present, a very high concentration of hydrogen and low concentrations of CO and CO₂. An explanation for this strange pattern is that the sieve column was full of air and it absorbed some quantities of CO and CO₂. The column was restored with a new absorbing

material. It was purged with helium and reconnected to the GC. A possible explanation of the high levels of hydrogen could be since helium and hydrogen have very close molecular weight the GC recognized helium as hydrogen. We can see that at 3:36 there is a peak in both graphs, this is the time that we were changing the column. From 3:36 to 4:08 p.m. is the time that we used to analyze the composition of the exit gas. After analyzing the exit gas we determined that 24% of our feed was gasified (figure #9). The amount of biomass gasified was less because the temperature in the reactor bed was lower than the first experiment.

After the experiment we performed a solids mass balance and analyzed the exit products. Figure #10 reports in which parts of the system the solids were recovered and their composition. The total feed was 2.9 Kg and we produced around 0.6 Kg of syngas. We recovered a total of 834.40 g of solids.

For our third experiment we used the MBMS to analyze tars and minor component of the syngas, in this experiment we didn't make a mass balance. Figures #14 to #20 show the variation in composition with changes of parameters. Figure #12 and #13 show the composition of the exit gas with the GC. In this experiment we had problem determining the composition of carbon monoxide, because the GC didn't detect carbon monoxide. The MBMS doesn't detect carbon monoxide, because it has the same molecular weight as nitrogen. With the other compounds we can see that the hydrogen intensity is too small, which means that the MBMS wasn't detecting it (figure #14). In figure #15 shows that during the process there were oxygen presented, and in a gasification process oxygen is supposed to be oxidized. Figure #16 shows that the composition of carbon dioxide remained almost constant. We varied the amount of oxygen that we put, so the amount of carbon dioxide should vary because of the combustion

reaction. The others components analyzed shown in figures #17to #21 show a strange pattern that needs more studying for complete understanding.

Discussion and Conclusions

The results obtained from the gasification of lignin in a fluidized bed reactors shows that hydrogen, carbon monoxide and the amount of feedstock gasified increase with increasing temperature. We can see this effect in the first experiment when the heater controller was not operating properly. On a dry gas volume basis, hydrogen is the dominant product within the temperature range studied, reaching a yield of around 20% and 35% by volume in the producer gas at 600 C and 700 C, respectively.

Another aspect to take in consideration is the moisture content of the feedstock, for the first experiment the pellets had a moisture content of 13% and in the second experiment the moisture content was 27%. The effect of the temperature and the moisture content can be seen comparing the amount of feedstock gasified; 41% and 21% in the first and second experiment, respectively.

One of our problems of this experiment was to pelletized and to lower the moisture content of our biomass. We did it with using a meat grinder and a dryer oven. Using this method we reduced the moisture content of 78% to 13%.

Mineral contents of fuel that remain in oxidized form after combustion is called ash. After analyzing the composition of our feedstock, we determined that it consisted of 40% ash. Since one undesirable product from the gasification process is ash, because it has impact on smooth running of gasifier, we determined that gasification is not a profitable option for the consumption of the residues of the biomass-to-ethanol conversion.

Acknowledgements

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References

- Bhattacharya, S.C. A study on wood gasification for low tar production. *Energy*, 24: 285-296; 1999
- Brage, Claes. Tar evolution profile obtained from gasification of biomass and coal. *Biomass and Bioenergy*, 18: 87-91; 2000
- Gil, Javier. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. *Biomass and Bioenergy*, 17: 389-403; 1999
- Knight, Richard. Experience with raw gas analysis from pressurized gasification of biomass. *Biomass and Bioenergy*, 18: 67-77; 2000
- Mansaray, K.G., Ghaly, A.E., Taweel, A.M. Air gasification of rice husk in a dual distributor type fluidized bed gasifier. *Biomass and Bioenergy*, 17: 315-332; 1999
- Miccio, F. Generation and conversion of carbonaceous fine particles during bubbling fluidized bed gasification of a biomass fuel. *Fuel*, 78: 1473-1481; 1999
- Rapagna, Sergio. Steam gasification of almond shells in a fluidized bed reactor: the influence of temperature and particle size on product yield and distribution. *Biomass and Bioenergy*, 12 (4): 281-288; 1997
- Warnecke, Ragnar. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. *Biomass and Bioenergy*. 18: 489-497; 2000

Figures

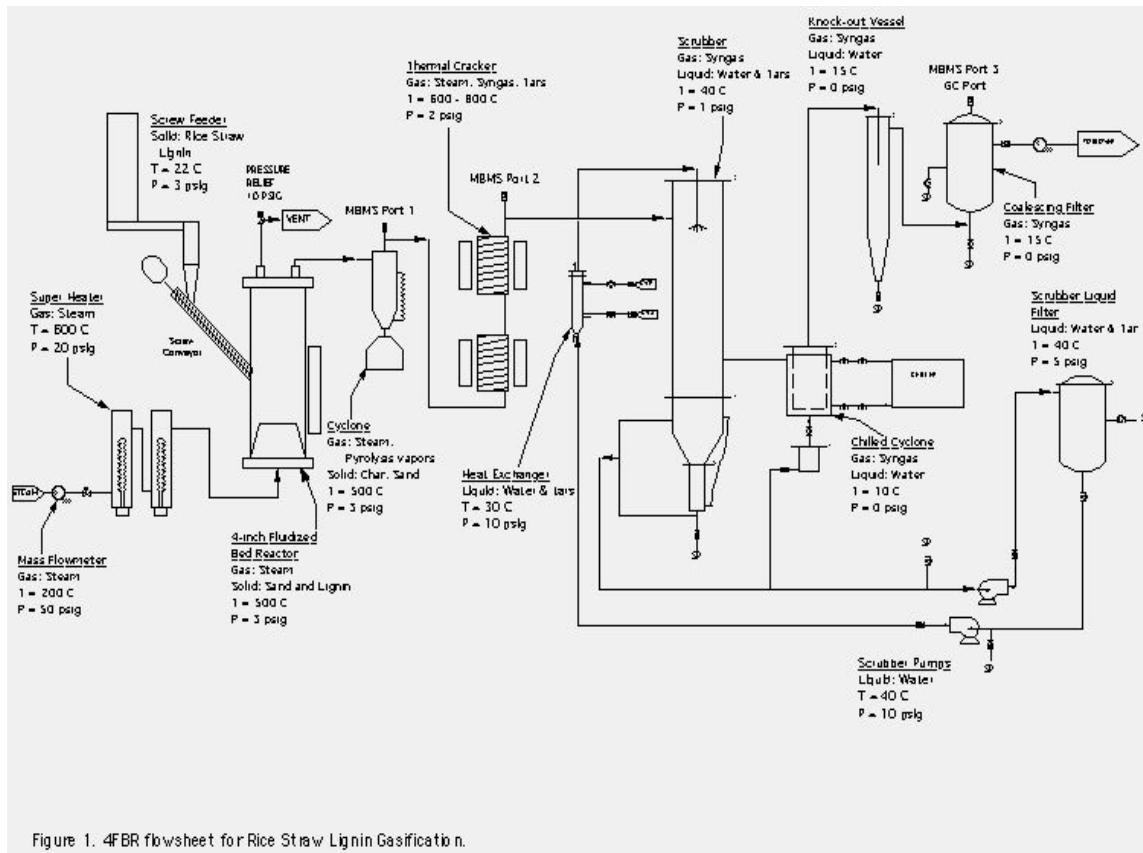


Figure 1. 4FBR flowsheet for Rice Straw Lignin Gasification.

Figure 2: Temperature profile of the first experiment

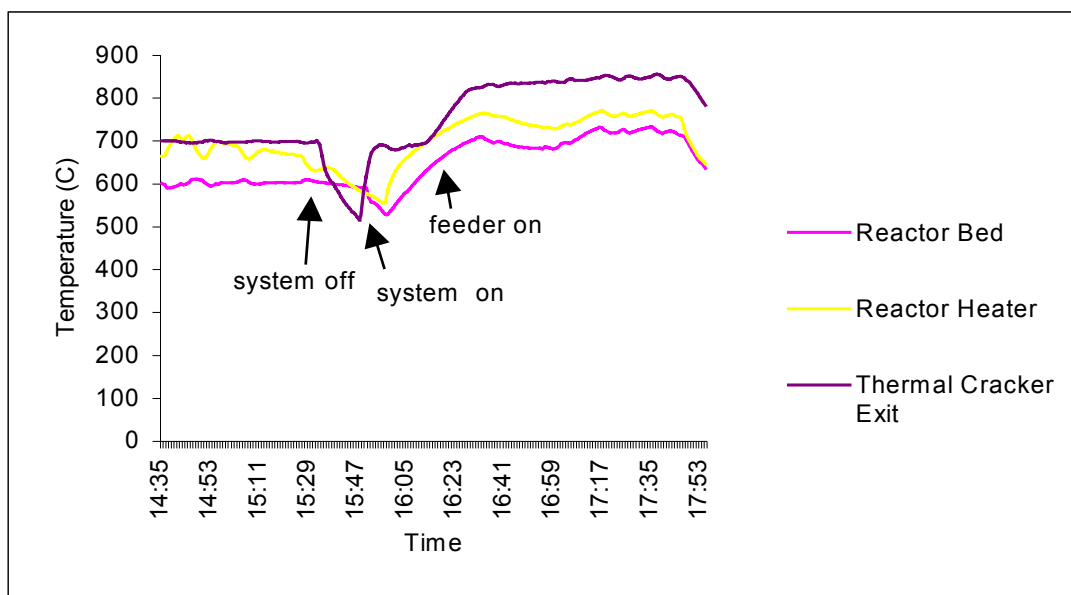


Figure 3: Formation of CO₂, CO, & H₂ in experiment #1

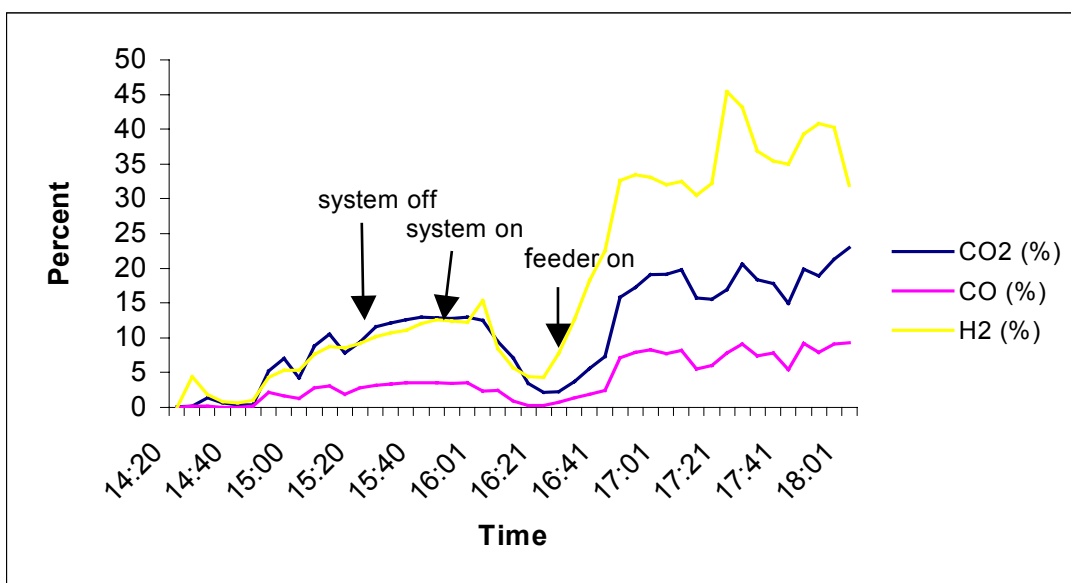


Figure 4: Formation of C_2H_6 , C_2H_2 , C_2H_4 & CH_4 in experiment #1

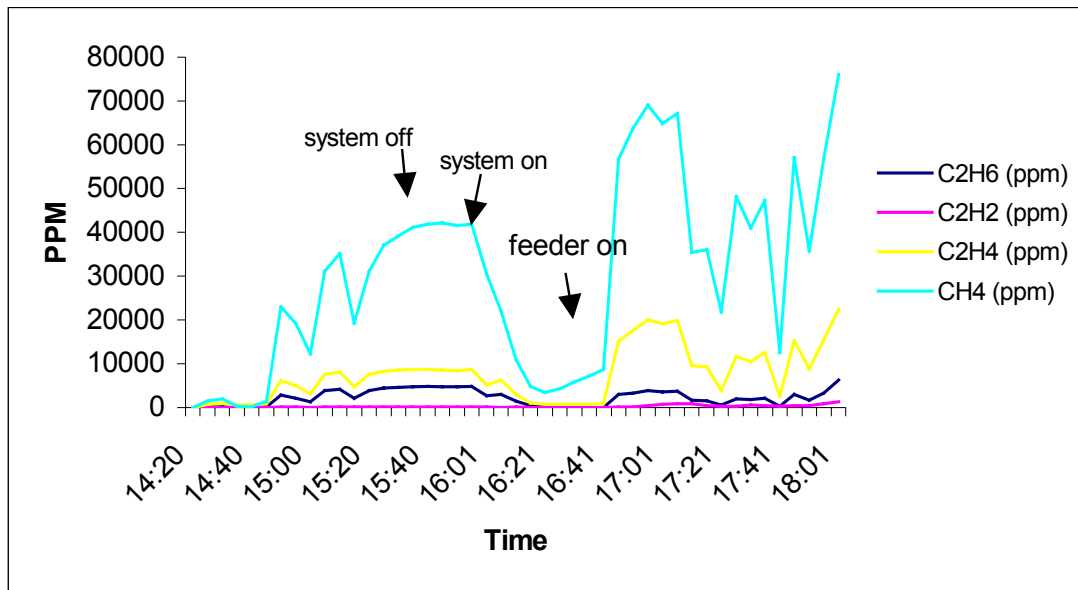


Figure 5: Amount of solids gasified in the first experiment

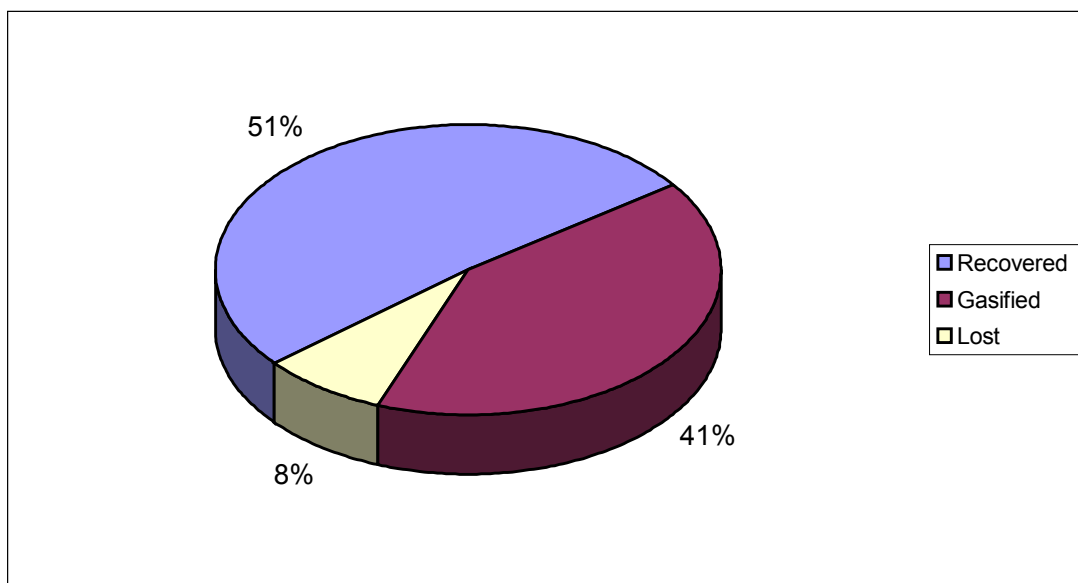


Figure 6: Temperature profile of experiment #2

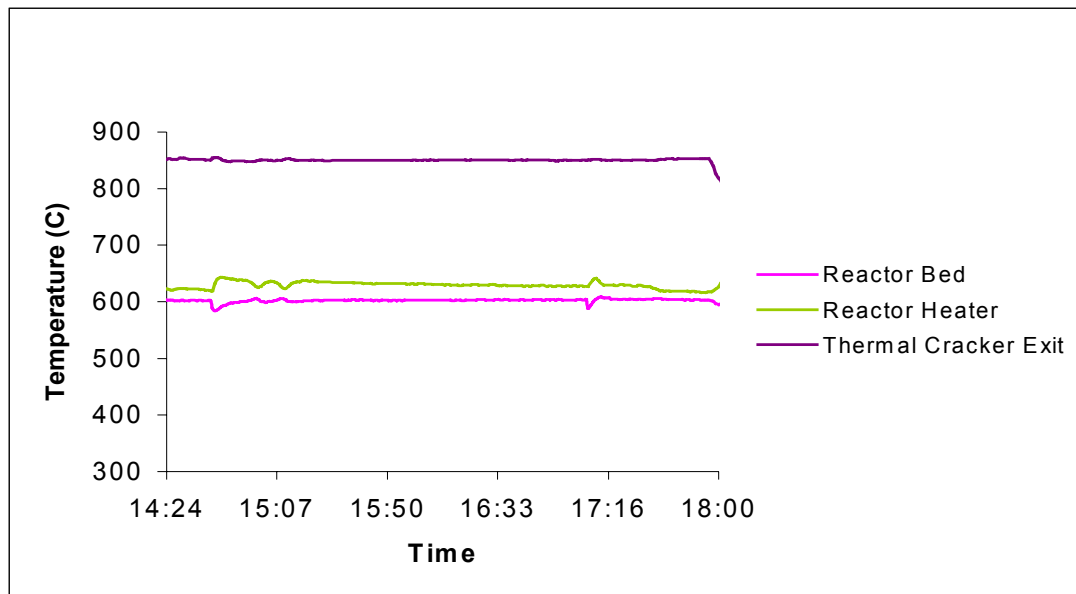


Figure 7: Formation of CO₂, H₂ and CO in Experiment #2

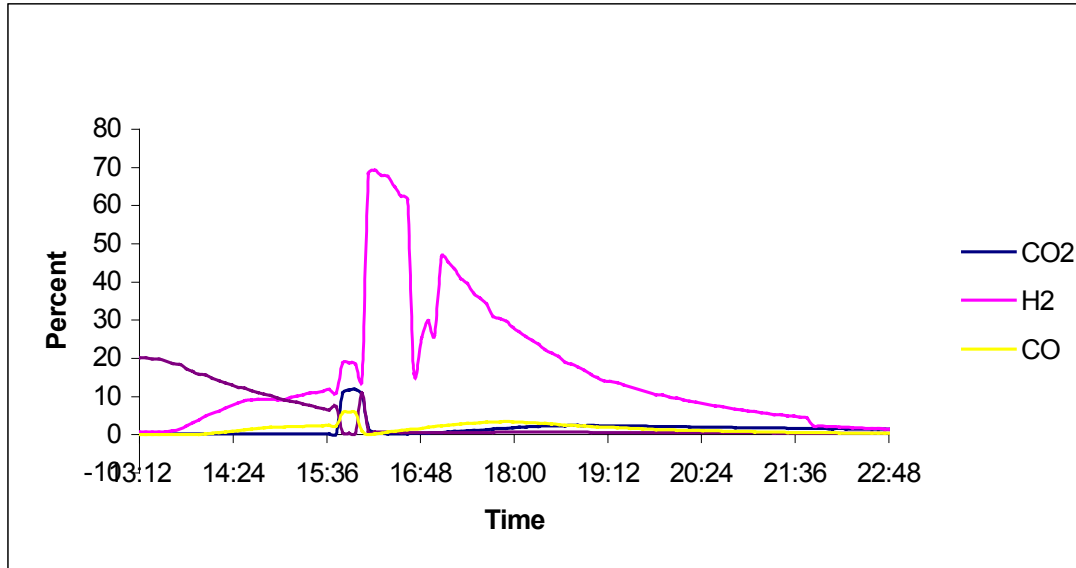


Figure 8: Formation of C₂H₄, C₂H₆, C₂H₂ & CH₄ in Experiment #2

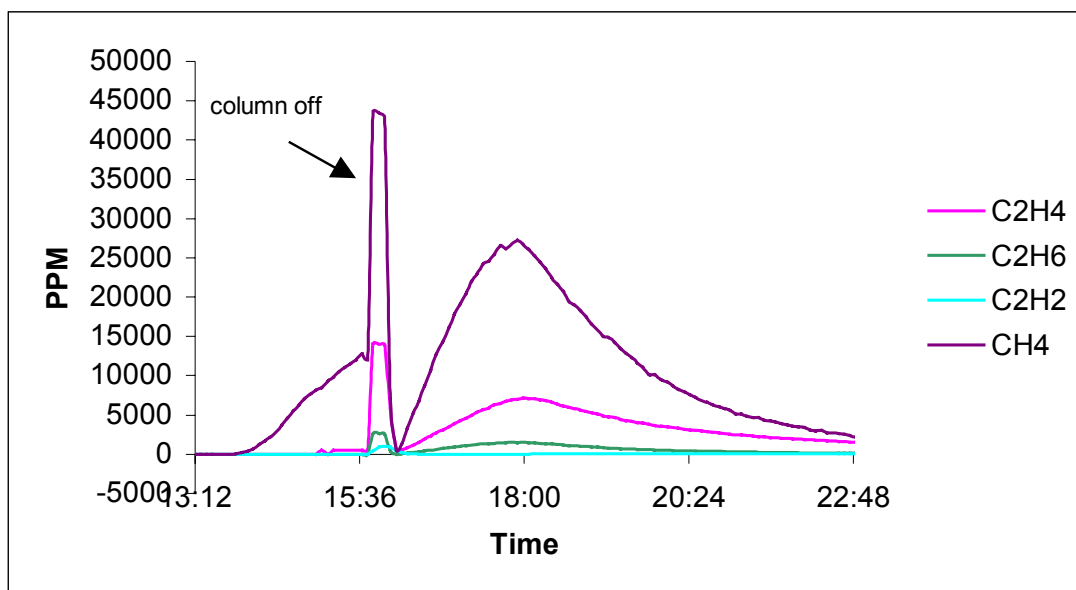


Figure 9: Amount of solids gasified in experiment #2

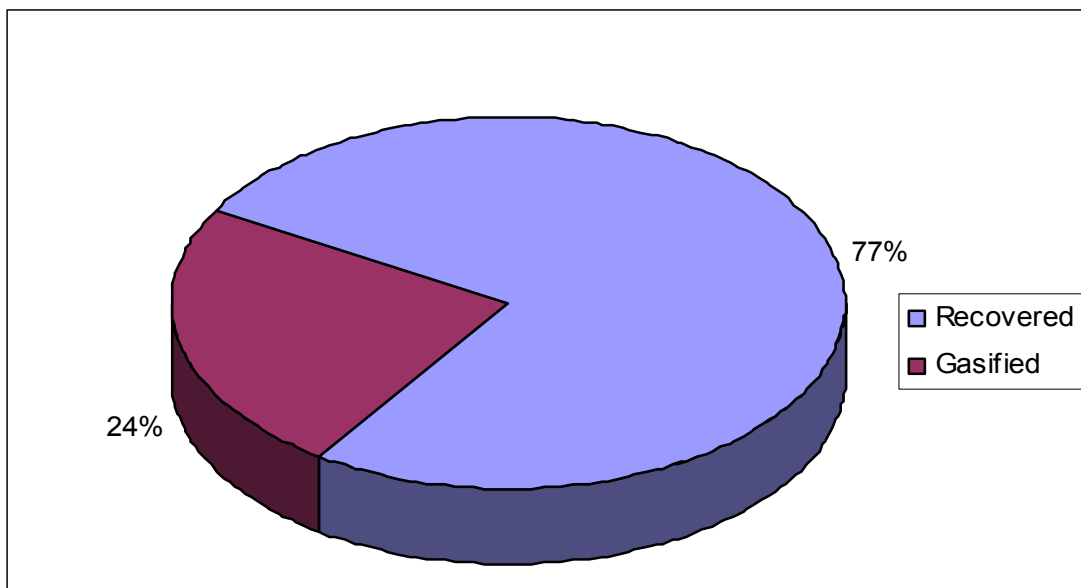


Figure 10: Mass Balance for Experiment #2

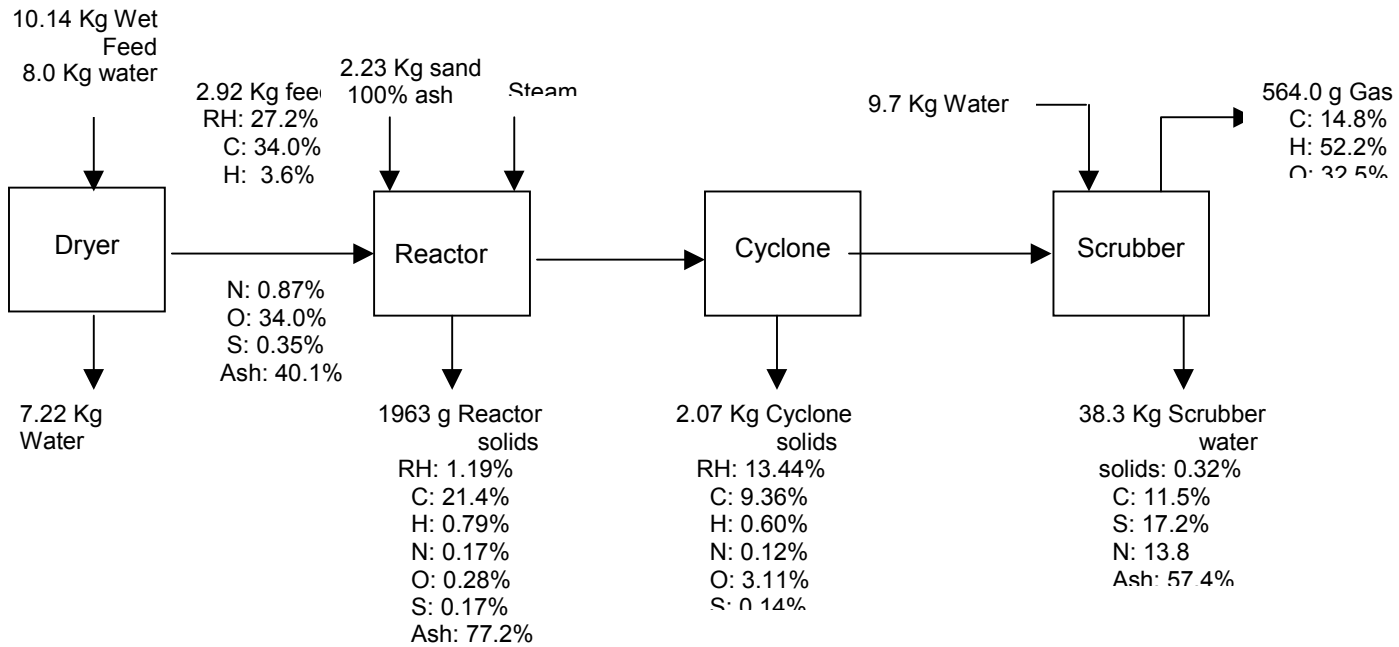


Figure 11: Temperature profile of experiment #3

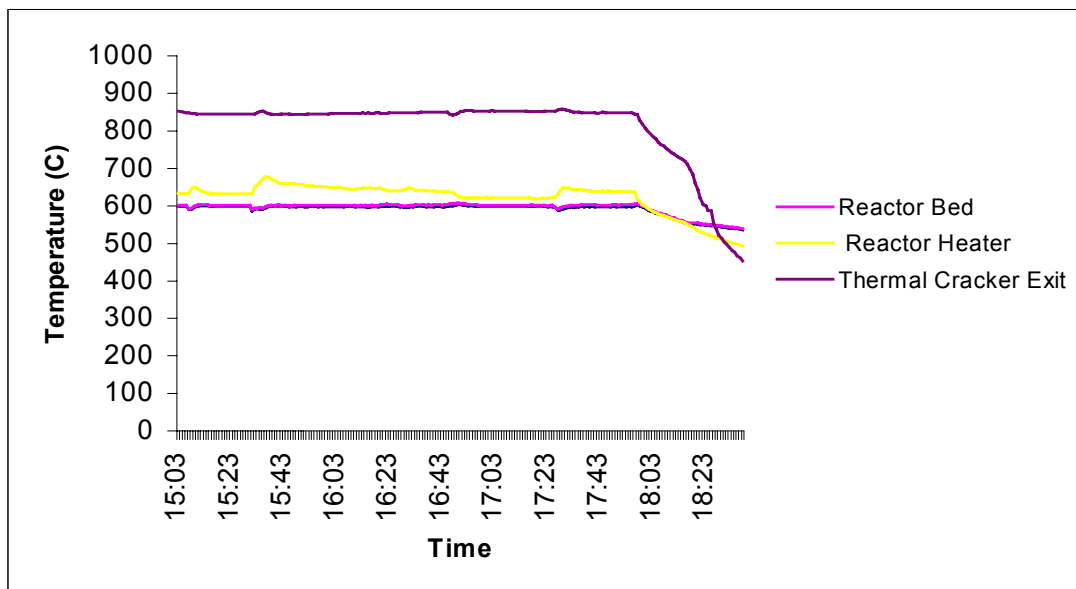


Figure 12: Formation of CO₂, H₂, CH₄ & O₂ in Experiment #3

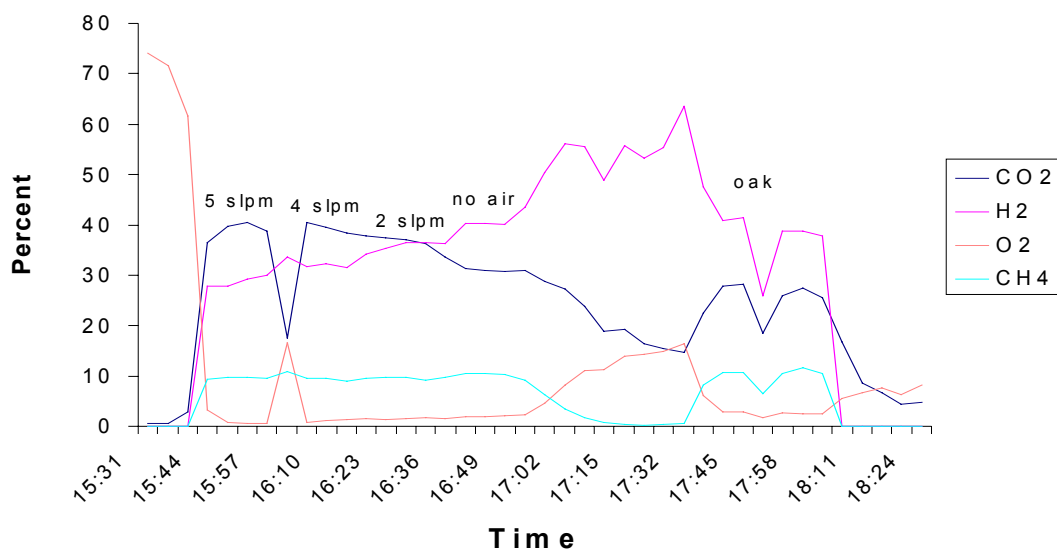


Figure 13: Formation of C₂H₄, C₂H₂ & C₂H₆ in Experiment #3

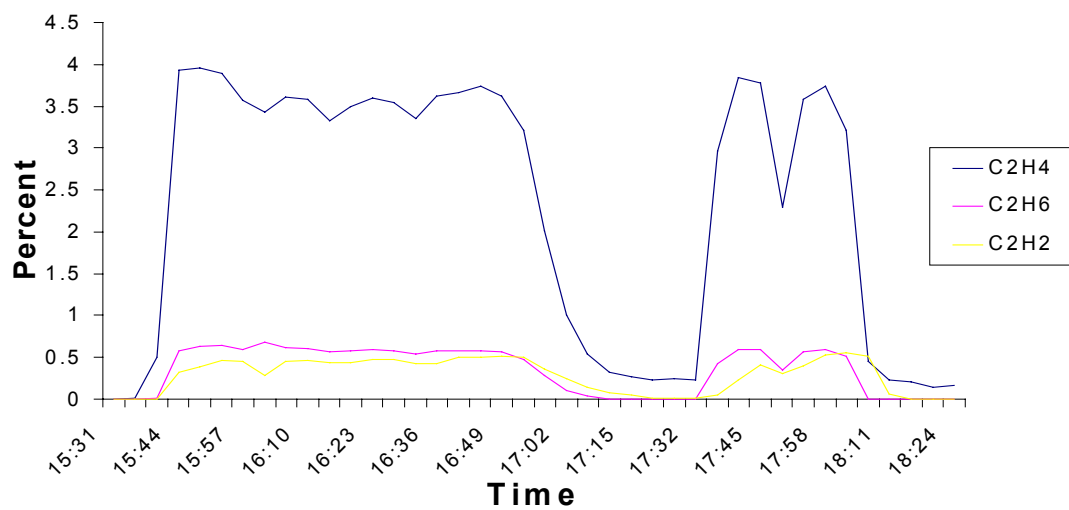


Figure 14: Average Intensity of Hydrogen

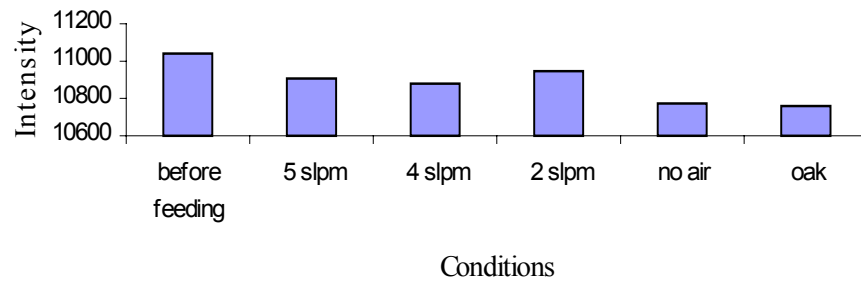


Figure 15: Average Intensity of Oxygen

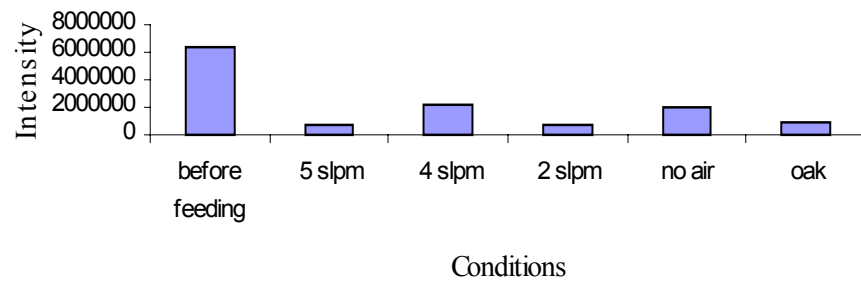


Figure 16: Average Intensity of Carbon Dioxide

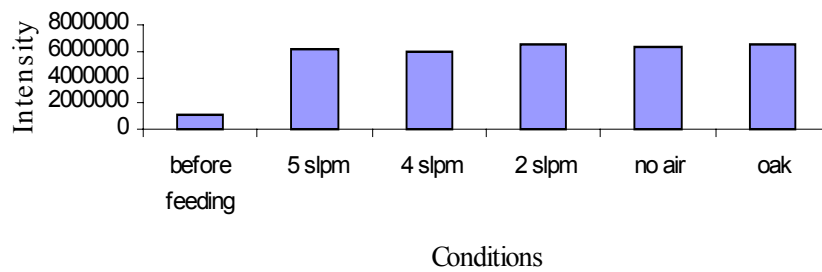


Figure 17: Average Intensity of Methane

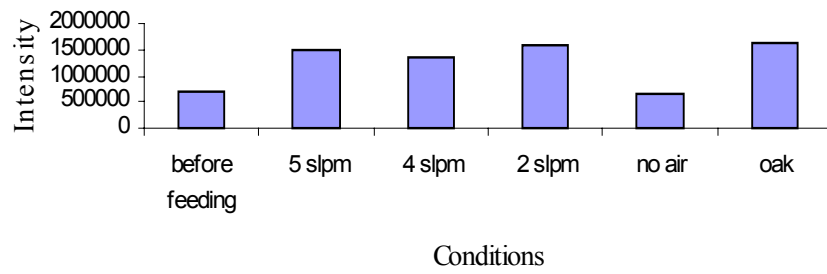


Figure 18: Average Intensity of Benzene

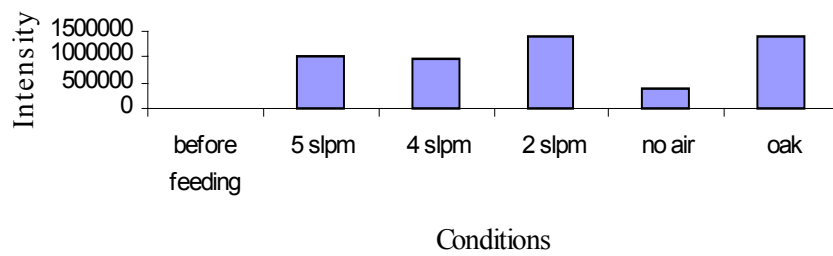


Figure 19: Average Intensity of Naphthalene

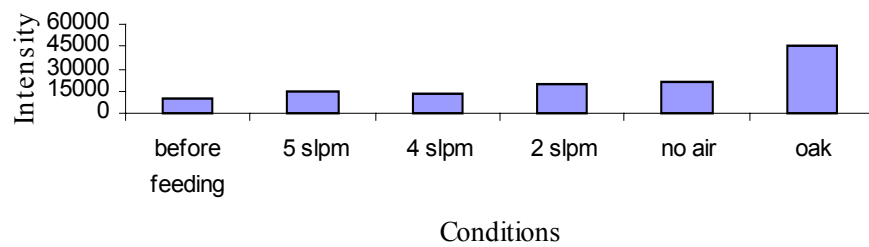


Figure 20: Average Intensity of Toluene

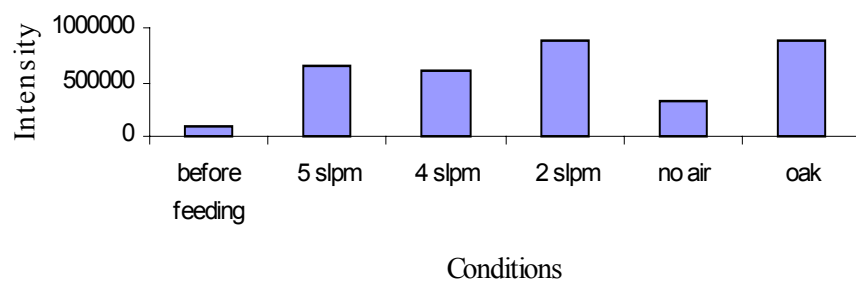
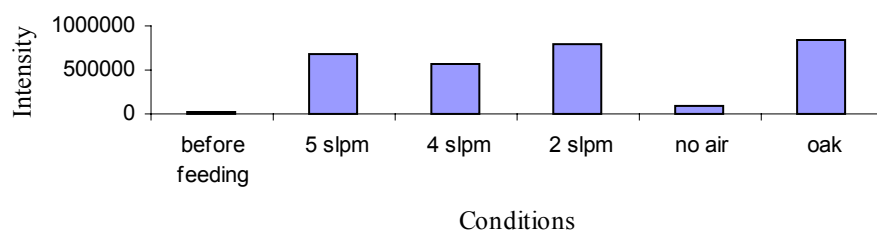


Figure 21: Average Intensity of Acetylene



Tables

Table 1: Mass Balance of the Solids in Experiment #1

Feed in the System	1765.70 g
Additional Solids in the reactor	181.40 g
Solids in the water Filter	112.10 g
Solids in the Gas Filter	5.30 g
Chilled cyclone residues	5.20 g
Knockout pot residues	0.40 g
Solids in the Cyclone	530.00 g
Total solids at the end	834.40 g

Table 2: Mass balance of water in Experiment #2

Total Water at the beginning	34956.24 g
Recovered Dirty Water	28522.80 g
Water on Water Filter	703.20 g
Water on Gas Filter	23.00 g
Cyclone Water	403.2 g
Water in Cyclone Char	59.10 g
Total water at the end	29711.30 g

Table 3: Mass Balance of the Solids in Experiment #2

Feed in the System	2928.80 g
Additional Solids in the reactor	268.0 g
Solids in the water Filter	569.00 g
Solids in the Gas Filter	10.40 g
Chilled cyclone residues	5.00 g
Knockout pot residues	0.00 g
Solids in the Cyclone	1942.20 g
Total solids at the end	2794.6 g

Table 4: Mass Balance of the Water in Experiment #2

Total Water at the beginning	42559.65 g
Recovered Dirty Water	38343.00 g
Water on Water Filter	232.40 g
Water on Gas Filter	0.00 g
Total water at the end	38575.40 g